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BENZENOID ORGANICS

HAZARDOUS WASTE SITE

SAMPLING

AND

ANALYSIS

GOVERNMENT DOCUMENTS
COLLECTION

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EXECUTIVE OFFICE OF ENVIRONMENTAL AFFAIRS

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BENZENOID ORGANICS HAZARDOUS WASTE SITE
SAMPLING AND ANALYSIS

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HISTORY:

The Benzenoid Organics site is located in Bellingham, Massachusetts on the banks of the Charles River impoundment Box Pond. The site has contained numerous manufacturing industries. Originally, the building was used as a woolen mill and then a leather processing plant prior to its 1964 occupation by Benzenoid Organics, a dye manufacturer. There are different reports on the type of dye Benzenoid Organics produced. A 1977 report stated intermediate dyes for Attleboro textile facilities were manufactured; a 1980 DEQE letter stated red dye #3; an FDA approved food dye was manufactured; and a 1980 consultant report stated red dye #2 and a "green-colored dye" were manufactured.

Residual wastes were disposed in eight lagoons located on the property. Most of the wastes were piped to the two closest lagoons, Lagoons 1 and 2, which overflowed to Lagoon 5, and eventually to Lagoon 7. When these lagoons were full, the pipes were extended so that the wastes could be discharged to Lagoon 3 which overflowed to Lagoons 4 and 6. Lagoon 8 was not connected to any other lagoons (see Figure 1).

In 1980 the DEQE Central Regional Office investigated the site and collected water and soil samples from the lagoons and nearby "Whites" Brook. The site was found to be in violation of the Hazardous Waste Regulations and DEQE told Benzenoid (Organics) Realty to hire a consulting firm to study the area and recommend proper closure of the lagoons.

In 1981, after an extensive study, the site was closed. Two feet of sediment from the walls and floors of lagoons 3, 4, 6, 7 and 8 were excavated and placed in Lagoons 1, 2 and 5. Lagoons 1, 2 and 5 were first treated using lime hydrate and sodium silicate. These were added to the walls and floor to chemically immobilize the metallic constituents and to develop a low permeability barrier below the sediments.

Once the sediments from Lagoons 3, 4, 6, 7 and 8 were placed and compacted into Lagoons 1, 2 and 5, the area was treated with hydrated lime and sodium silicate solution (to immobilize the metals in an alkaline environment). The area was then covered with about two feet of on-site glacial till and compacted.

PAST STUDIES:

IEP, Inc. Consultants conducted extensive sediment and water sampling to study the site (before closure) in February 1981. The results of their sampling indicated high metal concentrations in the sediment and various volatile organics in the groundwater. IEP took one to four different soil samples at each lagoon; several different depths sampled at each location. Samples were analyzed for % moisture, chromium, copper, lead, nickel, zinc and arsenic. The top foot of soil generally had the highest concentrations of metals. In particular, Lagoons 1, 2 and 5 had higher concentrations than the remaining lagoons. The only metal in concentrations of any significance was chromium. The highest chromium was observed in the surface samples and several stations had concentrations greater than 10,000 mg/kg.

IEP, Inc. also took water samples from both groundwater monitoring wells and the tributary to Box Pond "Whites" Brook. These samples were analyzed for VOA's,

chloride, iodide, sodium, arsenic, nickel, chromium, zinc, lead and copper. Metal concentrations were fairly low, but sodium, chloride and iodide concentrations were all high. The groundwater samples had sodium as high as 1700 mg/l, chloride as high as 2550 mg/l and iodide as high as 2920 mg/l. (Iodine was one of the ingredients used in the dye.)

The groundwater volatile organic water samples showed high concentrations of chlorobenzene and low concentrations of benzene, toluene and xylene.

In September 1984 the DEQE Central Office, Division of Hazardous Waste took soil and water samples from the lagoons, monitoring wells and tributary at the Benzenoid Organics site. This sampling was conducted as a follow-up to monitor the effectiveness of the closure and determine if problems still exist. Water samples were analyzed for VOA's, acid extractables, and lead and chromium. Soil samples were analyzed for lead and chromium. The soil samples did not appear to have high concentrations of lead or chromium. The metal concentrations in the water were low, but since hardness was not measured it is difficult to determine if they exceed the EPA proposed criteria. The groundwater, however, did have high concentrations of chlorobenzene and bis (2-ethylhexyl) phthalate. Chlorobenzene was also present in a red puddle on the stream bank, but not in the brook water.

CURRENT STATUS

The Benzenoid Organics site is being re-evaluated by the Division of Hazardous Waste. There still appears to be visible discoloration on the banks of the brook. Bright red and fluorescent green colored puddles can be observed leaching from the banks to the brook ("Whites" Brook, a tributary to Box Pond). In the winter, snow along the banks of the river has allegedly turned pink from the leaching dyes. There is concern that the metals and organics are still leaching into Box Pond and creating toxic or hazardous conditions.

Data, however, indicates that the metals do not appear to be traveling in the groundwater from the lagoons to the brook. Chlorobenzene is present in the groundwater, but it appears to volatilize as it reaches the air, and concentrations in the brook are negligible and not detected.

One parameter of concern may be the high concentrations of iodide in the groundwater. Iodide is soluble in water and through photochemical oxidation can be converted to iodine. Iodine is only slightly soluble with a structure similar to chlorine; it is often used as a disinfectant. Eight (8) mg/l of iodine is used to destroy waterbourne pathogens. Iodine tablets are often used to make water potable. The 1980 water samples had iodide concentrations ranging from a high of 2920 mg/l in a monitoring well adjacent to the lagoons down to a low of 11.2 mg/l in the brook's surface water. In 1984, there was no analysis for iodine.

SAMPLING

The Benzenoid Organics site was sampled on Monday, June 20, 1988. Three groundwater, six surface water and six sediment stations were sampled. These are listed in Table 1 (Figure 1).

GROUNDWATER STATIONS

There are five groundwater wells on-site that were installed in 1980 during a site study prior to closure. Well B-1 is located west of the lagoons, upgradient of the site. Well B-2 is located east and downgradient of the lagoons. This well was dry and thus was not sampled. Well #3 is located 100 feet east of Well B-2 and the lagoons on the banks of "Whites" Brook. There are two wells located at Well #3, a shallow well B-3S, less than 10 feet deep and a deep well B-3D, greater than 10 feet deep. The fourth well, B-4, was on the east bank of the brook. The cap could not be removed, and thus no sample was taken.

The three wells (B-1, B-3S, B-3D) were completely emptied of water using a stainless steel bailer. The wells were then left to recharge with new groundwater before sampling. Each well was sampled for metals and volatile organics.

The two wells adjacent to the brook had colored groundwater. The shallow well groundwater had a pink-red color and the deep well had a fluorescent green color.

SURFACE WATER STATIONS

Six surface water stations along "Whites" Brook were sampled for metals and volatile organics. Three of these stations were also tested for toxicity (the Microtox™ test) and were further sampled for chemical and nutrient parameters. "Whites" Brook is a small stream approximately three feet wide and half-a-foot deep.

The first station, W-1, was located upstream of the site where "Whites" Brook flows under the driveway.

This was sampled as the clean upstream station. The second Station W-2, was located in "Whites" Brook adjacent to Wells B-3S and B-3D. The stream had a slight pink color. Twenty feet downstream of Station W-2, there was a breakout of fluorescent green dye from the banks of the river to the brook. Station W-3 was located at the breakout. Station W-4 was approximately 20 feet downstream of W-3 at an area where red dye was leaching from the banks. The banks of the brook between Stations W-2 and W-4 had organic soil with no streamside vegetation and occasional red or green puddles.

Station W-5 was located approximately 50 feet downstream of W-4. The banks still contained organic soil, but tall grass and poison ivy was covering the ground. The brook was a dark "pink-red" color. The last Station W-6, was taken at the outlet of the brook to Box Pond. The brook went from a wooded path into cattails and the sample was taken as the brook entered the cattails.

Samples for Microtox™ analysis were taken at Stations W-1, W-4 and W-6.

SEDIMENT STATIONS

Six sediment samples were taken, four from the brook's stream bed and two from the floor of a former lagoon. Each station was analyzed for metals and for volatile organics.

Sediment samples from the brook were taken from the surface with a petite Ponar dredge. The stations were located at the same site as the surface water stations. Sediment sample S-1 was taken upstream at W-1, sample S-3 was taken at the green breakout W-3, sample S-4 was taken at the red breakout W-4, and sample S-5 was taken at the outlet W-6. The samples were fairly sandy. Stations S-3 and S-4 appeared slightly more organic than the other stations.

The two sediment samples from the lagoon were taken using a coring device. The samples were taken from a spot on Lagoon 3 where the soil was red and no vegetation was growing.

Sample S-2S was collected at the surface and sample S-2D was taken at a depth of one foot.

Samples were iced and transported the same day to the DEQE Lawrence Experiment Station for analysis. Iodide samples were sent to the EPA-NERL, Lexington for analysis.

DATA RESULTS

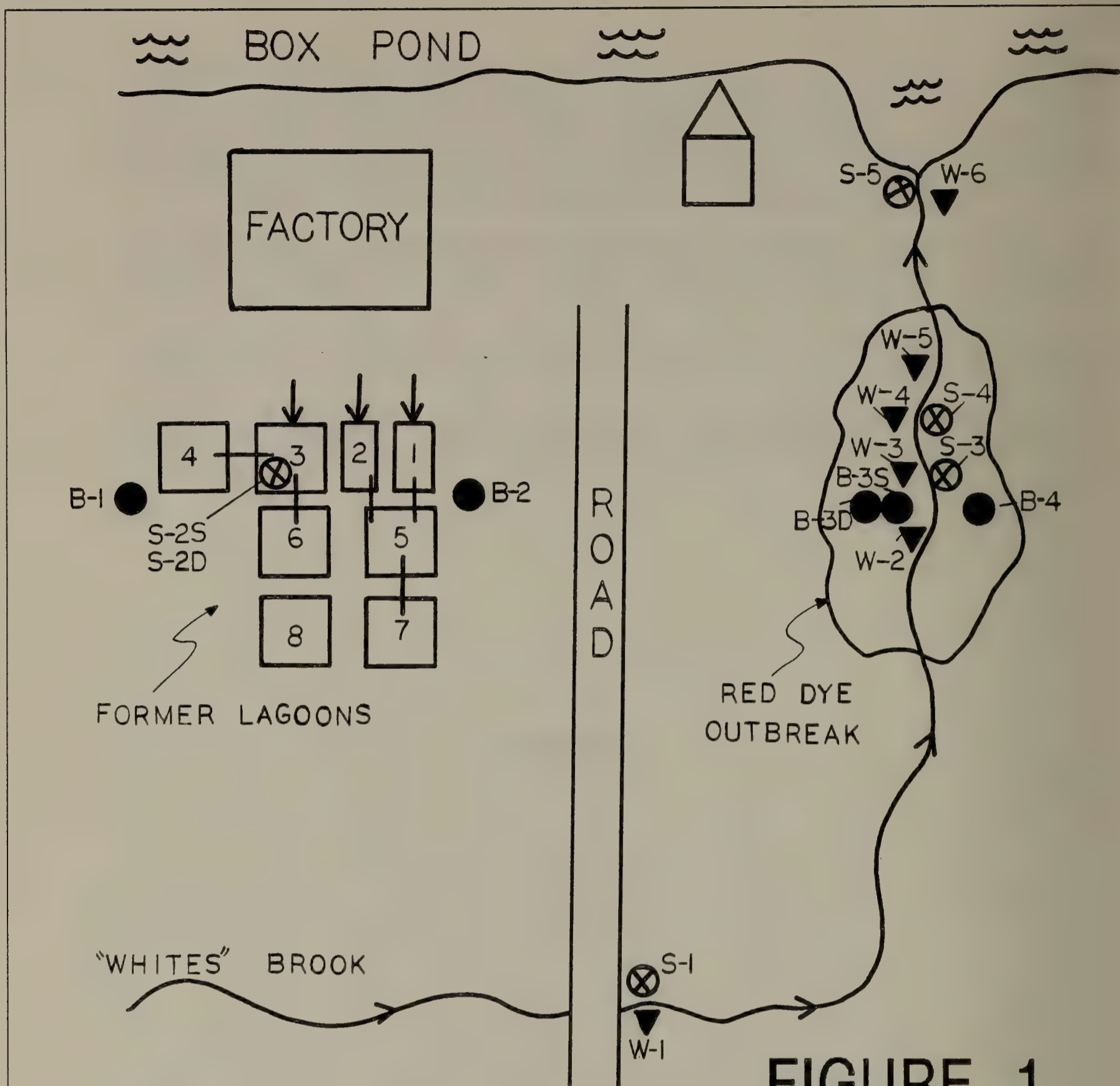


FIGURE 1

KEY

● GROUNDWATER WELL

▼ BROOK SAMPLE

⊗ SEDIMENT SAMPLE

Location of Sampling Stations

BENZENOID ORGANICS

Hazardous Waste Site

TABLE 1
LOCATION OF SAMPLING STATIONS

STATION	LOCATION
<u>GROUNDWATER</u>	
B-1	Upgradient clean well
B-3S	Shallow Well #3
B-3D	Deep Well #3
<u>SURFACE WATER</u>	
W-1	Clean upstream site where brook flows under driveway
W-2	Brook adjacent to Wells B-3S and B-3D
W-3	Twenty feet downstream of W-2 at breakout of fluorescent green dye
W-4	Twenty feet downstream of W-3, red dye leaching to brook
W-5	Fifty feet downstream of W-4, pink-red water
W-6	Outlet of brook to Box Pond where brook flows into cattails
<u>SEDIMENT</u>	
S-1	Clean upstream station, same as W-1
S-2S	Lagoon surface sample
S-2D	Lagoon sample at one-foot depth
S-3	Sediment with green dye leaching out, same as Station W-3
S-4	Sediment with red dye, same as Station W-4
S-5	Sediment at brook's outlet to Box Pond, same as Station W-6

TABLE 2
BENZENOID GROUNDWATER SAMPLE RESULTS

PARAMETER	B-1	B-3S	B-3D
<u>Metals (mg/l)</u>			
Hardness	44	18	11
Iodide	0.5	14.5	16.9
Aluminum	20.0	21.0	21.0
Cadmium	0.004	0.002	0.004
Chromium	0.29	0.33	2.7
Copper	0.21	0.09	0.32
Iron	920.0	120.0	480.0
Lead	0.55	0.065	0.18
Manganese	20.0	1.3	4.0
Mercury	0.0006	<0.0002	0.0003
Nickel	0.17	0.03	0.06
Zinc	1.6	0.46	0.99
<u>Volatile Organics (ug/l)</u>			
Benzene	-	1.6	3.7
Chlorobenzene	-	18	29
Ethyl benzene	-	2.8	3.3
Isopropyl benzene	-	7.9	7.8
N-propyl benzene	-	-	22
Sec-butyl benzene	-	-	*
Methyl ethyl etone	L10	-	-
Toluene	-	-	L1
Xylene	-	-	2.3
Several unidentified compounds	-	*	*

*No standard available for quantification

L1 = Less than 1 ug/l

L10 = Less than 10 ug/l

TABLE 3

BENZENOID SURFACE WATER SAMPLE RESULTS
(All results in mg/l unless noted)

PARAMETER	W-1	W-2	W-3	W-4	W-5	W-6
<u>Metals (mg/l)</u>						
Hardness	20	22	60	23	27	24
Iodide	0.5	0.5	1.9	0.5	0.8	0.8
Aluminum	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cadmium	<0.001	<0.001	0.002	<0.001	<0.001	<0.001
Chromium	<0.002	<0.002	0.250	0.015	0.022	0.009
Copper	0.20	0.04	0.20	0.04	0.04	0.03
Iron	0.08	0.38	100.0	0.40	0.68	0.43
Lead	<0.002	<0.002	0.12	<0.002	0.003	0.006
Manganese	0.04	0.08	1.8	0.09	0.08	0.13
Mercury	0.0006	<0.0002	0.01	0.0003	<0.0002	<0.0002
Nickel	0.001	0.009	0.050	0.009	0.009	0.009
Silver	0.02	-	-	-	<0.001	<0.001
Zinc	0.02	0.02	0.35	0.02	0.12	0.08
<u>Volatile Organics (ug/l)</u>						
	Sample lost	ND*	ND	ND	ND	ND

*ND = None detected

- Not analyzed

TABLE 4

"WHITES" BROOK WATER QUALITY RESULTS
(All results in mg/l unless noted)

PARAMETER	W-1	W-4	W-6
pH (Standard Units)	6.1	6.4	6.6
Total Alkalinity	8.0	13	15
Hardness	20	23	24
Suspended Solids	4.0	11	4.5
Total Solids	78	110	120
Spec. Conductivity (umhos/cm)	144	198	206
Total Kjeldahl-Nitrogen	0.33	0.30	0.32
Ammonia-Nitrogen	0.03	0.05	0.06
Dissolved Oxygen	9.8	8.1	7.7
Temperature (°C)	17	19	21

TABLE 5
BENZENOID SEDIMENT SAMPLE RESULTS

PARAMETER	S-1	S-2S	S-2D	S-3	S-4	S-5
<u>Metals (mg/kg)</u>						
Chromium	4.0	170	18	31	19	5.5
Copper	5.0	38	12	65	70	39
Iron	3,500	4,350	2,200	10,000	21,500	3,500
Lead	34	5.5	4.0	14	12	13
Manganese	65	35	18	80	170	47
Mercury	0.19	0.09	0.18	0.39	0.06	0.11
Nickel	3.0	<1.5	<1.5	3.0	8.5	3.0
Zinc	39	21	7.5	33	120	29
Volatile Solids(%)	12	1.7	0.5	3.5	4.6	7.5
<u>Volatile Organics (ug/g)</u>						
1,2-Dichloroethylene	<0.25	-	-	-	-	-
Toluene	-	<0.25	<0.25	0.35	1.2	0.70

ANALYSIS

METALS ANALYSIS

Water quality samples were analyzed for metals (I, Al, Cd, Cr, Cu, Fe, Pb, Mn, Ni, Zn) and hardness. Hardness is caused by divalent metallic cations, primarily calcium and magnesium, although other metals such as iron and manganese can contribute. Hardness concentrations are used to determine the toxicity criteria for heavy metals. The U.S. EPA has developed criteria and guidelines for the toxicity of metals based on hardness. These criteria are established to protect aquatic life, and are determined by the following equation:

$$\text{Criteria (ug/l)} \leq \exp [a \ln (\text{hardness in mg/l}) + b]$$

Values of a and b for each metal can be found in Table 6. The criteria are very low, and on occasion are below the laboratories detection limit. Thus, the effect on aquatic life maybe unknown.

In general, as hardness increases, the toxicity of the metal decreases, and the effect of the metal on the aquatic organisms is less. The average hardness of the water in "Whites" Brook is approximately 23 mg/l. Table 7 lists the criteria for water with a hardness of 20 and 25 mg/l (as CaCO₃).

Although some metals had concentrations below detection, most metals were above the detection limit. Several metals exceeded the EPA recommended criteria for the protection of aquatic life at least once. Copper exceeded the recommended criteria at every station.

Groundwater

The groundwater wells had the highest concentrations of metals (see Table 2). Well B-1, allegedly the upgradient well, had the highest observed concentrations of iron, lead, manganese, nickel and zinc. Cadmium, chromium and copper concentrations were also elevated. The "clean" upgradient well is not as clean as suspected.

Wells B-3S and B-3D also had higher concentrations of all the metals than the surface water samples. The water in the deep well had a green color and the water in the shallow well had a pink-red color. Every metal had a slightly higher concentration in the deep well than in the shallow well. The green, deeper groundwater appeared more contaminated than the pink colored groundwater.

Surface Water

The surface water stations (Table 3) had much lower metal concentrations than the groundwater stations. The "clean" upstream Station W-1 had surprisingly high concentrations of copper and mercury compared to the downstream stations. Station W-2 (adjacent to the two groundwater wells) had the lowest metal concentrations of the surface water stations.

The highest instream metals were found at Station W-3 located at the fluorescent green outbreak. The metal concentrations were all elevated similar to the green water in Well B-3D, but at a lower concentration due to dilution. The only exception was with mercury. A high mercury concentration of 0.01 mg/l was observed at Station W-3.

TABLE 6

U.S. EPA PROPOSED FRESHWATER CRITERIA FOR SELECTED
HEAVY METALS DESIGNATED TO PROTECT AQUATIC LIFE¹

<u>METAL</u>	4-DAY AVERAGE		ONE-HOUR AVERAGE	
	<u>a²</u>	<u>b²</u>	<u>a²</u>	<u>b²</u>
Cadmium	0.7852	-3.49	1.128	-3.828
Chromium III	0.8190	1.561	0.8190	3.688
Copper	0.8545	-1.465	0.9422	-1.464
Lead	1.273	-4.705	1.273	-1.460
Mercury	(0.012 ug/l)		(2.4 ug/l)	
	24-HOUR AVERAGE		AT ANY TIME NOT TO EXCEED	
	<u>a²</u>	<u>b²</u>	<u>a²</u>	<u>b²</u>
Nickel	0.76	1.06	0.76	4.02
Zinc	(47 ug/l)		0.83	1.95

¹ EPA "Quality Criteria for Water 1986," EPA 440/5-86-001, May, 1986.

² For input into: $\exp(a [\ln(\text{hardness in mg/l})] + b)$

TABLE 7

U.S. EPA PROPOSED FRESHWATER CRITERIA FOR SELECTED
METALS BASED ON A HARDNESS OF 20 AND 25 mg/l
(as CaCO₃)

<u>METAL HARDNESS</u>	<u>4-DAY AVERAGE</u>		<u>ONE-HOUR AVERAGE</u>	
	<u>20(mg/l)</u>	<u>25(mg/l)</u>	<u>20(mg/l)</u>	<u>25(mg/l)</u>
Cadmium	0.0003	0.0004	0.0006	0.0008
Chromium III	0.0554	0.2701	0.4648	0.5579
Copper	0.0030	0.0036	0.0039	0.0048
Lead	0.0004	0.0005	0.0105	0.0140
Mercury	0.00001		0.0024	
	<u>24-HOUR AVERAGE</u>		<u>AT ANY TIME NOT TO EXCEED</u>	
	<u>20(mg/l)</u>	<u>25(mg/l)</u>	<u>20(mg/l)</u>	<u>25(mg/l)</u>
Nickel	0.0281	0.0333	0.5428	0.6431
Zinc	0.0471	0.0470	0.0845	0.1017

Iron: 0.3 mg/l for domestic water supplies
1.0 mg/l for freshwater aquatic life

Manganese: 0.05 mg/l for domestic water supplies

As the brook flowed downstream, the mercury concentration decreased to 0.0003 mg/l 20 feet downstream and less than detection 50 feet downstream. The source of the mercury is unknown.

Iodine was sampled in the brook under the assumption it was one ingredient used in the manufacture of the red pigments. The highest iodide concentrations, however, were found instream at Station W-3 with the green dye breakout and in the deep well with the green colored groundwater. The highest instream iodide concentration was 1.9 mg/l and the highest groundwater concentration was 16.9 mg/l. The sample taken at the red dye outbreak (W-4) had one of the lowest concentrations of iodide at 0.5 mg/l.

Instream copper concentrations exceeded the one-hour average criteria of 0.0039 mg/l (20 mg/l hardness) at every station. The highest copper concentrations were at Station W-1 and W-3. Copper is known to be toxic to aquatic life.

Sediments

The metal concentrations in the sediment samples were fairly low (refer to Table 5). All of the heavy (toxic) metal concentrations were very low, well below the allowable concentration established in the Massachusetts classification of dredge or fill material. (see Table 8).

Percent volatile solids was also analyzed in each sediment. The higher the percent volatile solids, the higher the organic content of the sediment. Metals are more likely to adhere to organic particles than sandy particles. The sediment samples from "Whites" Brook and the lagoon were primarily sandy and thus had low percent volatile solids and low metal adsorptive abilities.

The lagoon was sampled twice (surface and one-foot depth) at an area where the soil was red and no vegetation was growing. The lagoon surface sample had slightly higher metal concentrations than the deeper sediment sample for all metals except mercury.

The sediment samples taken from the brook had low metal concentrations. The clean upstream sediment had higher lead, manganese and zinc concentrations than the other brook stations. This station is located at the end of a culvert which flows under the driveway and could receive runoff from the road, causing the elevated lead and zinc. Furthermore, sample S-1 had a higher percent volatile solids (12%) than the remaining stations indicating more adsorptive capacity for metals.

VOLATILE ORGANIC ANALYSIS (VOA)

Volatile organic water samples were taken from the six surface water and three groundwater stations, and six volatile organic sediment samples were taken from the four river and two lagoon stations. Samples were taken in 240 ml vials with teflon caps and filled so that no air space was present.

Groundwater and surface water samples were analyzed according to the EPA procedure "Method 624-Organics by Purge and Trap." Sediment samples were analyzed according to the EPA procedure, Method 8240 Gas Chromatography Mass Spectrometry for Volatile Organics," SW-846 1B.

TABLE 8
CLASSIFICATION OF DREDGE OR FILL MATERIAL

314 CMR 9.03
(All units in mg/kg)

PARAMETER	CATETORY ONE	CATEGORY ONE	CATEGORY ONE
Arsenic (As)	<10	10-20	>20
Cadmium (Cd)	<5	5-10	>10
Chromium (Cr)	<100	100-300	>300
Copper (Cu)	<200	200-400	>400
Lead (Pb)	<100	100-200	>200
Mercury (Hg)	<0.5	0.5-1.5	>1.5
Nickel (Ni)	<50	50-100	>100
Polychlorinated Biphenyls (PCB)	<0.5	0.5-1.0	>1.0
Vanadium (V)	<75	75-125	>125
Zinc (ZN)	<200	200-400	>400

Groundwater

Trace levels of volatile organics were detected in the groundwater. The upgradient Well B-1 had a trace amount of methyl ethyl ketone, which was not detected in the down gradient wells. The shallow and deep down gradient Wells B-3S and B-3D had low levels of benzene and various benzene derivatives (Table 1). The highest concentration was chlorobenzene at 29 ug/l in the deep well and 18 ug/l in the shallow well. The deeper well had more organics and higher concentrations than the shallow well.

The EPA "Quality Criteria for Water 1986" (EPA 44015-86-001 May 1986) gives the following recommended limits for benzene, ethyl benzene and toluene. (The other organics were not listed).

- Acute toxicity to freshwater aquatic life occurs at concentrations of:

Benzene - 5,300 ug/l
Ethyl benzene - 32,000 ug/l
Toluene - 17,500 ug/l

- Human health consumption is toxic at concentrations above:

Benzene - 6.6 ug/l, 0.66 ug/l, 0.060 ug/l for cancer risk of one in 10^{-5} ,
10⁻⁶, 10⁻⁷
Ethyl benzene - 1,400 ug/l
Toluene - 14,300 ug/l

- Human health consumption of aquatic organisms is toxic at concentrations above:

Benzene - 400 ug/l, 4.00 ug/l, 4.0 ug/l for cancer risk of one in 10^{-5} ,
10⁻⁶, 10⁻⁷
Ethyl benzene - 3,280 ug/l
Toluene - 424,000 ug/l

The concentrations observed in the wells were not high enough to cause toxicity to freshwater aquatic life or human consumption.

Benzene and its derivatives are volatile and when exposed to the air will evaporate out of the water. Groundwater has no dissolved oxygen and tends to hold compounds in their form.

Surface Water

No volatile organics were detected in any of the surface water stations. The groundwater had such low concentrations that when exposed to the air in the brook they would volatilize. Furthermore, the groundwater samples were received on June 20, 1988 and analyzed on August 20, 1988. Standard methods states VOA analyses should be conducted within 14 days of receipt. By being held for two months, any volatiles present may have left and the results would not be indicative of the true concentration. The groundwater samples were analyzed within two weeks of receipt.

Sediment

The lagoon and stream sediment samples (Table 5) also had very low concentrations of organics (all less than 1 ug/g). The lagoon was sampled at the surface and at a one-foot depth. Both samples had reported <0.25 ug/l of toluene. Downstream sediment samples (except Station S-1) had slightly higher toluene concentrations ranging from 0.25 ug/g to 1.2 ug/g. The sediment samples were analyzed August 24, 1988, two and one-half months after being received. This is also after the holding time and could indicate erroneous data.

MICROTOX™ TOXICITY TESTING RESULTS

Toxicity samples were taken at three locations along "Whites" Brook; at the upstream Station W-1; at the red dye outbreak Station W-4; and at the brook's outlet to Box Pond, Station W-6. The samples were tested for toxicity with the Microtox™ toxicity analyzer on June 21, 1988. Results are presented in Table 9.

Microtox™ is the trade name for a particular acute toxicity test. The Division of Water Pollution Control's Technical Services Branch currently uses the test as a toxics screening tool in addition to other, more traditional methods of analysis.

The Microtox™ analyzer uses freeze-dried luminescent bacteria as its test organisms. When re-hydrated, these bacteria emit light. To test a water sample for toxicity using Microtox™, an analyst prepares a series of dilutions of the sample and adds re-hydrated bacteria to these. The light intensity of each sample dilution is measured at pre-selected time intervals over a 30-minute period and compared with that of a control (bacteria only). It is assumed that changes in light intensity are due to toxicant interference with the biochemical reaction that produces light. Toxicity is then measured as the percent decrease in light intensity of each of the sample dilutions compared with that of the control.

The upstream Station W-1 did exhibit some incipient levels of toxicity with EC₁₀'s between 15.9 and 95.0% sample. This toxicity was observed to increase over time (5 to 30-minute reading). All other results were non-toxic, however, with EC₂₀'s and EC₅₀ all 100% sample.

Station W-4, which was next to the leachate outbreak area was virtually non-toxic to the Microtox™ bacteria. The single exception to this was the 30-minute EC₁₀'s reading of 73.0% sample.

The downstream Station W-6 exhibited the highest levels of incipient toxicity. Though no EC₅₀'s were obtained (100% sample) EC₁₀'s and EC₂₀'s ranged between 24.0 to 61.0% sample and 53.0 to 100% sample, respectively. The results indicated a persistent toxicant as the toxicity increased over time.

It was somewhat surprising that the background levels of incipient toxicity at Station W-1 exceeded those of Station W-4, and were only slightly less toxic than Station W-6. The downstream station, however, exhibited the highest levels of toxicity with EC₂₀'s between 53.0 and 100% sample (Station W-4 was adjacent to the leachate outbreak). If future work is scheduled at this site, it is recommended that a reference station at Mendon Street (Route 140) be added to

TABLE 9

BENZENOID MICROTOX™ ANALYSES RESULTS

STATION	TEST DURATION (Min.)	EC ₁₀	EC ₂₀	EC ₅₀
W-1	5	94.0%	>100%	>100%
	15	18.9%	>100%	>100%
	30	15.9%	>100%	>100%
W-4	5	>100%	>100%	>100%
	15	>100%	>100%	>100%
	30	73.0%	>100%	>100%
W-6	5	61.0%	>100%	>100%
	15	37.0%	82.0%	>100%
	30	24.0%	53.0%	>100%

*Results given as percent volume of sample.

determine the background level of incipient toxicity (if any) in "Whites" Brook. This could determine if Station W-1 has also been impacted by the Benzenoid Organics site.

COMPARISON OF PAST DATA

The Benzenoid organics site was initially sampled by IEP in 1981 as part of an intensive study of the site. The data reported extremely high concentrations of heavy metals in the soil and groundwater.

The site was closed and capped later in 1981. Then in 1984, the DEQE resampled the groundwater wells and stream to monitor the effectiveness of the closure. Although the data indicated concentrations of lead and chromium in the groundwater and sediment were lower, no other metals were analyzed. Furthermore, the red and green pigments continue to leach out of the banks of the brook and cause discoloration of the water. Thus, in 1988, a second follow-up survey was conducted.

It is difficult to compare data between the three surveys because variations in the parameters analyzed and sample locations varied from survey to survey.

Groundwater

It is not possible to compare data from every groundwater well for each survey. Well B-1 was only analyzed for iodide, sodium and chloride in 1981, was not sampled in 1984, and had VOA's and metals sampled in 1988. Similarly, Well B-4 had a complete VOA and metal scan in 1981, but was not sampled in 1984 or 1988.

The deep and shallow Wells B-3S and B-3D were sampled during all three surveys for VOA's and metals. The 1984 survey, however, only analyzed for lead and chromium. Comparisons are tabulated in Tables 10 and 11. From the data it appears that the concentrations of volatile organics in the groundwater have decreased. The chlorobenzene concentration in particular has decreased from 351 ug/l to 300 ug/l to 18 ug/l in the shallow well and from 189 ug/l to 150 ug/l to 29 ug/l in the deep well. While the other parameters also decreased, a number of new organics appeared in 1988 that were not detected earlier. These are the various benzene derivatives (i.e., ethylbenzene; isopropylbenzene, N-propylbenzene etc.). Possibly these are the result of the chlorobenzene parameters breaking down.

The metals data, however, appeared to increase in concentration over the three surveys, for all metals except iodide. In 1981, IEP determined the groundwater flow to be less than one-foot per year. Thus, the contaminated groundwater may be still traveling through the soil. The higher concentrations indicate that the problem has not been completely removed and some contamination still exists. The groundwater should continue to be monitored for metals and any dramatic increases noted. The lagoons are approximately 100 feet from the brook. Benzenoid organics began operating its dye manufacturing in 1964. If the groundwater velocity calculations of one-foot/year are correct, the most contaminated water will arrive at "Whites" Brook in 75 years. The current dye outbreaks are from groundwater traveling faster than one-foot/year. Unfortunately, Well B-2 was not sampled in 1984 and was dry during the 1988 survey, so no groundwater data between the former lagoons and the brook is available.

TABLE 10
COMPARISON OF GROUNDWATER VOA DATA
(All results in ug/l)

STATION	2/20/81	9/28/84	6/6/88
<u>Well B-1</u>			
Methyl ethyl etone	-	Not sampled	<10 ug/l
<u>Well B-3S</u>			
Benzene	9.4	11	1.6
Chlorobenzene	351	300	18
Isopropyl benzene	-	*	7.9
Toluene	2.1	2.2	-
Xylene	44	-	-
Ethyl benzene	-	-	2.8
Isopropyl benzene	-	-	7.9
Unidentified compounds	-	-	*
<u>Well B-3D</u>			
Pentane	-	*	-
Hexane	-	*	-
Benzene	7.1	3.3	3.7
Chlorobenzene	189	150	29
Toluene	2.5	-	<1
Xylene	18	-	2.3
Ethyl benzene	-	-	3.3
Isopropyl benzene	-	-	7.8
N-propyl benzene	-	-	22
Sec-butyl benzene	-	-	-
Unidentified compounds	-	-	*

* No standard available for quantification

TABLE 11

COMPARISON OF GROUNDWATER METAL DATA
(All results in mg/l)

STATION	2/18/81	9/28/84	6/20/88
<u>Well B-3S</u>			
Iodide	2070	-	14.5
Chromium	0.07	0.24	0.33
Copper	0.04	-	0.09
Lead	<0.1	0.07	0.065
Nickel	<0.05	-	0.03
Zinc	0.07	-	0.46
<u>Well B-3D</u>			
Iodide	1380	-	16.9
Chromium	0.07	0.40	2.7
Copper	0.02	-	0.32
Lead	<0.1	0.28	0.18
Nickel	<0.05	-	0.06
Zinc	0.06	-	0.99

Note: All other metals were only sampled once and have no other data to compare to.

Another item of note is that during the 1981 and 1984 surveys, the shallow well had higher metal and VOA concentrations than the deeper well. In 1988 the deeper well had higher concentrations. The 1981 and 1984 surveys were conducted at the end of February and the end of September, while the 1988 survey was conducted in June. The June survey may have been conducted during a lower groundwater table-level (Well B-2 was dry) than the other two surveys. A lower groundwater table could account for the higher concentrations in the deep well.

Surface Water

The surface water data between the three surveys is difficult to compare. In 1981, two surface water samples were taken and analyzed for sodium, chloride and iodide only. In 1984, there were numerous surface water stations, but the metals were only analyzed for lead and chromium. In 1988, the six surface water stations were analyzed for ten different metals and iodide. Thus, comparisons are limited. Furthermore, the exact locations of the sampling in 1981 and 1984 are unknown.

Sediment

The sediment sample data are also difficult to compare exactly, although general trends can be observed. In 1981, no sediment samples were taken from the brook and in 1984 four sediment samples were taken from the brook and analyzed for lead and chromium only. The exact location of these four stations is unknown, but the data can be compared to the 1988 Stations S-3 and S-4 which were taken in the same general vicinity. In 1984, the instream sediment lead concentrations were 23 mg/kg, 28 mg/kg, 22 mg/kg and 29 mg/kg. In 1988, the two sediment lead concentrations were 14 mg/kg and 12 mg/kg, less than 1984. Similarly, in 1984 the chromium concentrations were 87 mg/kg, 150 mg/kg, 120 mg/kg and 75 mg/kg respectively. The 1988 sediment chromium concentrations were 19 mg/kg and 31 mg/kg, considerably less than 1984.

The stream sediment metal concentrations appear to be decreasing. If the 1984 sediment composition was more organic than the sandy 1988 data, then the higher concentrations would be due to more binding sites. Percent volatile solids was not determined in 1984.

A comparison of the sediment data taken from lagoon #3 in 1981 and 1988 can be found in Table 12 (no data was taken in 1984). In 1981 numerous sediment samples at varying depths were taken from each lagoon. Samples were taken to a depth of two-feet deep. The metal concentrations reported were very high. During the closure process, the top two-feet of sediment were removed, buried and capped on-site.

In 1988 a sediment sample was taken at two different depths; surface, and one-foot, from former Lagoon #3. The comparison of the 1981 data and 1988 data provided information on "before" and "after" closure. Unfortunately, the 1981 data only went to a depth of two-feet. Allegedly, two-feet of soil was removed so the 1988 data does not have an identical "before" sample to compare to.

The 1988 surface data had concentration only slightly less than the 1981 two-foot sample for most metals. Thus, it appears that the metals in the soil may not have moved far. The 1988 data also had lower metal concentrations, one-foot below the surface than at the surface.

TABLE 12

COMPARISON OF LAGOON #3 SEDIMENT DATA
(All results in mg/kg)

PARAMETER	#1 - 1981		#2 - 1981		#3 - 1981		1988	
	0-6"	6"-2'	0-6"	6"-2'	0-6"	6"-2'	Surface	One-Foot
Chromium	650	720	106	118	315	39.8	170	18
Copper	510	200	40.0	42.5	187	78.6	38	12
Lead	12.0	15.0	5.0	<5.0	5.0	<5.0	5.5	4.0
Nickel	2.8	6.2	<0.5	<0.5	0.9	<0.5	<1.5	<1.5
Zinc	21.0	38.0	16.0	14.0	28.5	4.0	21	7.5

Volatile organics were only analyzed for in the sediments in 1988, thus no comparisons can be made.

CONCLUSION

The evaluation of the 1988 groundwater, surface water and sediment data indicates potential problems with metal concentrations in the groundwater and surface water and no to slight problems with volatile organics. When comparing the 1988 data to previous data, slight trends can be seen. It appears that the volatile organics concentrations in the groundwater and surface water are decreasing and are not at concentrations to produce toxicity to aquatic organisms.

Groundwater metal concentrations, however, have increased in concentration over the past seven years. If groundwater is moving at one-foot/year as predicted, then metal concentrations could continue to increase over the years. The upgradient groundwater well was contaminated with high concentrations of select metals. The groundwater could possibly be traveling in other directions. There are not enough wells to define the groundwater flow direction. If any drinking-water wells are located nearby, they should be analyzed for metals.

Surface water metal concentrations were slightly above the EPA recommended criteria. Copper in particular was at toxic concentrations. Instream toxicity samples had some toxicity that should be looked into further. Originally it was thought high iodide concentrations was causing the red color and toxicity. Iodide concentrations, however, were low and did not appear to be causing a problem.

The lagoon sediment samples had low metal concentrations. The samples were taken at a worst-case location at the only place where no vegetation was growing. Thus, the sediments appear stable and should not present a problem.

RECOMMENDATIONS

Based on the results of this study the following recommendations in regards to future actions at the site are presented:

- 1) Another round of sampling should occur to address the metal concentrations in the groundwater. This would involve sampling at a high groundwater table so a sample can be obtained from Well B-2. Also, Well B-4 should be sampled. If any other well (i.e., drinking-water supply) is nearby it should be sampled.
- 2) Toxicity tests should be rerun and an additional "clean" upstream site should be included. This could help evaluate if Station S-1 is being impacted by the site.
- 3) If volatile organics are ever sampled again, the 14-day holding period should be adhered to.
- 4) Core sediment samples should be taken from the stream to see if past contaminants are bound in the sediment below the surface.

